

PATENT SPECIFICATION

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(54) NOVEL BENZIMIDAZOLES AND THEIR USE AS FUNGICIDES AND BACTERICIDES

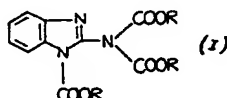
(71) We, BAYER AKTIENGESELLSCHAFT, a body corporate organised under the laws of Germany, of Leverkusen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to certain 1-alkoxycarbonyl-2-[bis-(alkoxycarbonyl)-amino]-benzimidazoles, to a process for their preparation and to their use as fungicides and bactericides.

It has been disclosed that 1-butylcarbamoyl-2-methoxycarbonyl-amino-benzimidazole possesses fungicidal, especially systemic fungicidal, properties (see United States Patent Specification 3,541,213).

Furthermore, it is known that 6-methyl-2,3-quinoxalinedithiol-cyclocarbonate (see German Auslegeschrift (German Published Specification) 1,100,372) and n-dodecylguanidine acetate (see United States Patent Specification 2,425,341) can be used as fungicides; the two last-mentioned active compounds have also attained practical importance as commercially available preparations.

The present invention provides 1-alkoxycarbonyl-2-[bis-(alkoxycarbonyl)-amino]-benzimidazoles of the general formula



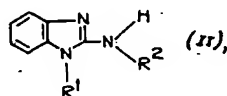
in which

R represents alkyl with 1—4 carbon atoms, it being possible for the radicals R to be different from one another or two or three radicals R to be identical.

It has been found that the benzimidazoles of the formula (I) display strong fungicidal, especially strong systemic fungicidal, and bactericidal properties.

Preferably R is methyl, ethyl, n-propyl, isopropyl or n-butyl.

The present invention also provides a process for the preparation of a 1-alkoxycarbonyl-2-[bis-(alkoxycarbonyl)-amino]-benzimidazole of the general formula (I), in which a 2-amino-benzimidazole of the general formula



in which

R¹ and R² are each hydrogen or a —COOR radical, and R has the above-mentioned meaning,

is reacted with a carbonic acid derivative of the general formula



(III),

[Price 33p]

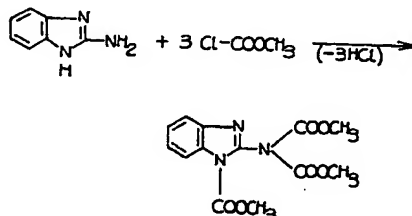
in which

X is halogen (preferably chlorine) or an —O—COOR radical, and R has the above-mentioned meaning,

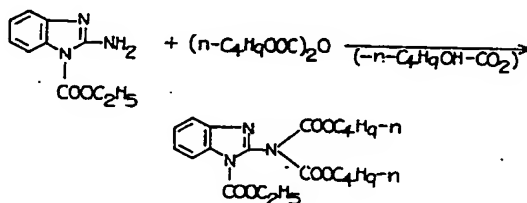
optionally in the presence of a diluent and optionally in the presence of an acid-binding agent.

Surprisingly, the 1-alkoxycarbonyl-2-[bis-(alkoxycarbonyl)-amino]-benzimidazoles according to the invention display a substantially greater fungicidal action, especially a substantially greater systemic fungicidal action, than 1-butylcarbamoyl-2-methoxycarbonyl-amino-benzimidazole known from the state of the art, which is chemically the nearest commercially available product of the same type of action. In addition, the active compounds according to the invention possess bactericidal properties towards bacteria in crop farming. The compounds according to the invention thus represent an enrichment of the art.

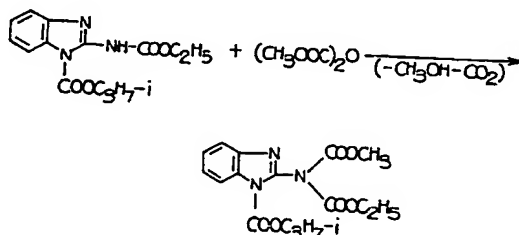
If 2-amino-benzimidazole and chlorocarbonic acid methyl ester are used as starting materials, the course of the reaction can be represented by the following equation:



If 1-ethoxycarbonyl-2-amino-benzimidazole and pyrocarbonic acid di-n-butyl ester are used as starting materials, the course of the reaction can be represented by the following equation:



If 1-isopropoxycarbonyl-2-ethoxycarbonyl-amino-benzimidazole and pyrocarbonic acid dimethyl ester are used as starting materials, the course of the reaction can be represented by the following equation:



The 2-amino-benzimidazoles of the formula (II) which can be used according to the invention are largely known; the compounds of the formula (II) which are not yet known can be prepared according to known processes (see United States Patent Specification 2,933,502 and 2,933,504).

The following may be mentioned as examples of the compounds of the formula (II): 2-amino-benzimidazole, 1-methoxycarbonyl-2-amino-benzimidazole, 1-ethoxycarbonyl-2-amino-benzimidazole, 1-propoxycarbonyl-2-amino-benzimidazole, 1-isopropoxycarbonyl-2-amino-benzimidazole and 1-butoxycarbonyl-2-amino-benzimidazole; 2-methoxycarbonylamino-benzimidazole, 2-ethoxycarbonylamino-benzimidazole, 2-propoxycarbonylamino-benzimidazole, 2-

isopropoxycarbonylamino - benzimidazole and 2 - butoxycarbonylamino - benzimidazole; 1 - methoxycarbonyl - 2 - methoxycarbonylamino - benzimidazole, 1 - ethoxycarbonyl - 2 - ethoxycarbonylamino - benzimidazole, 1 - propoxycarbonyl - 2 - propoxycarbonylamino - benzimidazole, 1 - isopropoxycarbonyl - 2 - isopropoxycarbonylamino - benzimidazole, 1 - butoxycarbonyl - 2 - butoxycarbonylamino - benzimidazole, 1 - methoxycarbonyl - 2 - ethoxycarbonylamino - benzimidazole, 1 - ethoxycarbonyl - 2 - methoxycarbonylamino - benzimidazole, 1 - isopropoxycarbonyl - 2 - ethoxycarbonylamino - benzimidazole and 1 - butoxycarbonyl - 2 - propoxycarbonylamino - benzimidazole.

The halogenocarbonic acid alkyl esters of the formula (III) which can be used according to the invention are known (see Beilstein's Handbuch der Organischen Chemie (Beilstein's Handbook of Organic Chemistry), Edition IV, 3rd supplementary work, volume 3, pages 23 to 26). As examples there may be mentioned: chlorocarbonic acid methyl ester, chlorocarbonic acid ethyl ester, chlorocarbonic acid propyl ester, chlorocarbonic acid isopropyl ester and chlorocarbonic acid butyl ester.

The pyrocarbonic acid dialkyl esters of the formula (III) which can be used according to the invention are also known or can be prepared in a known manner (see Liebigs Ann. Chem. 624 (1959), pages 30—36). As examples there may be mentioned: pyrocarbonic acid dimethyl ester, pyrocarbonic acid diethyl ester, pyrocarbonic acid dipropyl ester, pyrocarbonic acid diisopropyl ester and pyrocarbonic acid dibutyl ester.

As diluents it is possible to use polar solvents which are inert towards the carbonic acid derivatives of the formula (III). These include, for example, heterocyclic bases, such as pyridine and alkylpyridines, quinoline and alkylquinolines as well as isoquinoline, and also commercially available technical mixtures of these solvents. The following may be mentioned as being particularly suitable: pyridine, 2-methyl-pyridine, 3-methyl-pyridine, 4-methyl-pyridine, 4-ethyl-pyridine, 2-methyl-5-ethyl-pyridine, the isomeric lutidines and collidines, quinoline, 2-methyl-quinoline, 4-methyl-quinoline, 6-methyl-quinoline and iso-quinoline.

Pyridine is the preferred solvent, especially when carbonic acid derivatives of the formula (III) in which X is an —O—COOR radical (pyrocarbonic acid esters) are used.

All customary acid-binders can be employed as acid-binding agents. These include inorganic bases, such as alkaline earth metal hydroxides, for example calcium hydroxide or barium hydroxide, alkali metal carbonates or alkaline earth metal carbonates, such as sodium carbonate, potassium carbonate and calcium carbonate, and organic bases, such as tertiary amines, for example triethylamine, N,N -dimethylaniline, pyridines, quinolines and isoquinolines. It is particularly appropriate to use pyridine, lutidines or quinoline as the acid-binding agent since these bases can also at the same time be regarded as particularly suitable solvents; thus, pyridine is the most preferred acid-binding agent.

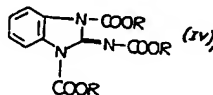
The reaction temperatures can be varied over a fairly wide range. In general, the reaction is carried out at from -10° to 100°C , preferably from 10° to 50°C .

The reactions can be carried out not only under normal pressure but also under elevated pressure. In general, normal pressure is used.

Usually, in carrying out the process according to the invention, 3 to 4.5 moles of carbonic acid derivative of the formula (III) are employed per mole of the 2-amino-benzimidazole of the formula (II) wherein R^1 and R^2 represent hydrogen. 2 to 3.5 moles of a carbonic acid derivative of the formula (III) are usually employed per mole of the 2-amino-benzimidazole of the formula (II), wherein either R^1 or R^2 is a —COOR radical. 1 to 2.5 moles of a carbonic acid derivative of the formula (III) are usually employed per mole of the 2-aminobenzimidazole of the formula (II), wherein R^1 and R^2 both represent a —COOR radical.

In general, 500 to 750 ml of an organic base, preferably pyridine, which optionally can be used simultaneously as the acid-binding agent, are employed per mole of the 2-amino-benzimidazole of the formula (II).

Working up takes place in the usual manner. The reaction products are crystalline and can optionally be purified by recrystallisation. In particular, the isomeric 2-imino-benzimidazolines of the structure



which may arise as by-products, can easily be separated off and identified, according to customary processes (see the preparative examples herein).

The following may be mentioned as typical examples of the active compounds which can be prepared according to the invention: 1 - methoxycarbonyl - 2 - [bis - (methoxycarbonyl) - amino] - benzimidazole, 1 - ethoxycarbonyl - 2 - [bis - (ethoxycarbonyl) - amino] - benzimidazole, 1 - propoxycarbonyl - 2 - [bis - (propoxycarbonyl) - amino] - benzimidazole, 1 - butoxycarbonyl - 2 - [bis - (butoxycarbonyl) - amino] - benzimidazole, 1 - methoxycarbonyl - 2 - (N - methoxycarbonyl - N - ethoxycarbonyl - amino) - benzimidazole, 1 - methoxycarbonyl - 2 - (N - methoxycarbonyl - N - isopropoxycarbonyl - amino) - benzimidazole, 1 - methoxycarbonyl - 2 - (N - methoxycarbonyl - N - butoxycarbonyl - amino) - benzimidazole, 1 - ethoxycarbonyl - 2 - (N - methoxycarbonyl - N - ethoxycarbonyl - amino) - benzimidazole, 1 - ethoxycarbonyl - 2 - (N - ethoxycarbonyl - N - propoxycarbonyl - amino) - benzimidazole, 1 - ethoxycarbonyl - 2 - [bis - (methoxycarboxyl) - amino] - benzimidazole, 1 - methoxycarbonyl - 2 - [bis - (ethoxycarbonyl) - amino] - benzimidazole, 1 - methoxycarbonyl - 2 - (N - ethoxycarbonyl - N - isopropoxycarbonyl - amino) - benzimidazole and 1 - isopropoxycarbonyl - 2 - (N - methoxycarbonyl - N - ethoxycarbonyl - amino) - benzimidazole.

The active compounds according to the invention show a strong fungitoxic and bacteriotoxic action. They do not harm crop plants in the concentrations required for combating fungi and bacteria and have a low toxicity towards warm-blooded animals. For these reasons, they are suitable for use as plant protection agents for combating fungi and bacteria. Fungitoxic agents are employed in plant protection for combating *Archimycetes*, *Phycomycetes*, *Ascomycetes*, *Basidiomycetes* and *Fungi Imperfecti*.

The active compounds according to the invention have a very broad spectrum of action and can be used against parasitic fungi and bacteria which attack above-ground parts of plants or attack the plants through the soil, and against seed-borne pathogens.

The active compounds show a high systemic activity, especially against those fungi which cause powdery mildew diseases. This group of fungi predominantly includes representatives of the family of the Erysiphaceae, the most important genera being *Erysiphe*, *Uncinula* (*Oidium*), *Sphaerotheca* and *Podosphaera*. The following may be mentioned as important fungi: *Erysiphe cichoracearum*, *Podosphaera leucotricha* and *Uncinula necator*. The action against powdery mildew fungi can also be achieved by using the substances by the seed dressing process.

The compounds according to the invention, however, are also active against other fungi which attack crop plants such as, for example, *Cochliobolus myiabeanus*, *Mycosphaerella musicola*, *Cercospora personata*, *Botrytis cinerea*, varieties of *Alternaria*, *Verticillium alboatrum*, *Phialophora cinereascens* and varieties of *Fusarium*, as well as against the bacterium *Xanthomonas oryzae*.

The active compounds according to the present invention can be converted into the usual formulations, such as solutions, emulsions, suspensions, powders, pastes and granulates. These may be produced in known manner, for example by mixing the active compounds with extenders, that is, liquid or solid or liquefied gaseous diluents or carriers, optionally with the use of surface-active agents, that is, emulsifying agents and/or dispersing agents and/or foam-forming agents. In the case of the use of water as an extender, organic solvents can, for example, also be used as auxiliary solvents.

As liquid diluents or carriers, there are preferably used aromatic hydrocarbons, such as xylenes, toluene, benzene or alkyl naphthalenes, chlorinated aromatic or aliphatic hydrocarbons, such as chlorobenzenes, chloroethylenes or methylene chloride, aliphatic hydrocarbons, such as cyclohexane or paraffins, for example mineral oil fractions, alcohols, such as butanol or glycol as well as their ethers and esters, ketones, such as acetone, methyl ethyl ketone, methyl isobutyl ketone or cyclohexanone, or strongly polar solvents, such as dimethyl formamide, dimethyl sulphoxide or acetonitrile, as well as water.

By liquefied gaseous diluents or carriers are meant liquids which would be gaseous at normal temperatures and pressures, for example aerosol propellants, such as halogenated hydrocarbons, for example Freon (registered trade mark).

As solid diluents or carriers, there are preferably used ground natural minerals, such as kaolins, clays, talc, chalk, quartz, attapulgit, montmorillonite or diatomaceous earth, or ground synthetic minerals, such as highly-dispersed silicic acid, alumina or silicates.

Preferred examples of emulsifying and foam-forming agents include non-ionic and anionic emulsifiers, such as polyoxyethylene-fatty acid esters, polyoxyethylene-fatty alcohol ethers, for example alkylaryl polyglycol ethers, alkyl sulphonates, alkyl sulphates and aryl sulphonates as well as albumin hydrolyzation products; and preferred examples of dispersing agents include lignin sulphite waste liquors and methyl cellulose.

The active compounds according to the invention can be present in the formula-

tions as mixtures with other active compounds, such as other fungicides, insecticides and acaricides.

The formulations generally contain from 0.1 to 95 per cent, preferably from 0.5 to 90 per cent, by weight of active compound.

The active compounds can be used as such, in the form of their formulations or in the application forms prepared therefrom, such as ready-to-use solutions, emulsifiable concentrates, emulsions, suspensions, wettable powders, pastes, soluble powders, dusting agents and granules. They can be used in the customary manner, for example by spraying, fumigating, gassing, watering, dressing or encrusting.

The active compound concentrations in the ready-to-use preparations can be varied within fairly wide ranges. In general, they are from 0.0001 to 10%, preferably from 0.01 to 1%, by weight.

The active compounds can also be used with good success in the ultra-low-volume (ULV) method, where it is possible to apply formulations of up to 95% active compound or even to use the active compound by itself.

When used as seed dressings, amounts of 0.1 to 10 g of active compound, preferably of 0.2 to 2 g, per kg of seed are generally employed.

When used as soil treatment agents, amounts of 1 to 500 g, preferably 10 to 200 g are generally to be employed per cubic metre of soil.

The present invention also provides a fungicidal or bactericidal composition containing as active ingredient a compound of the present invention in admixture with a solid or liquefied gaseous diluent or carrier or in admixture with a liquid diluent or carrier containing a surface-active agent.

The present invention also provides a method of combating fungi or bacteria which comprises applying to the fungi or bacteria or a habitat thereof a compound of the present invention alone or in the form of a composition containing as active ingredient a compound of the present invention in admixture with a diluent or carrier.

The present invention further provides crops protected from damage by fungi or bacteria by being grown in areas in which immediately prior to and/or during the time of the growing a compound of the present invention was applied alone or in admixture with a diluent or carrier. It will be seen that the usual methods of providing a harvested crop may be improved by the present invention.

The following test Examples are given by way of illustration.

Example A. *Erysiphe* test

Solvent: 4.7 parts by weight of acetone
Emulsifier: 0.3 part by weight of alkylaryl polyglycol ether
Water: 95 parts by weight

The amount of the active compound required for the desired concentration of active compound in the spray liquid was mixed with the stated amount of the solvent, and the concentrate was diluted with the stated amount of water containing the stated additions.

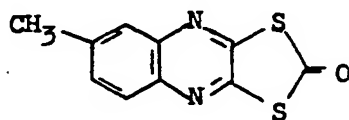
Young cucumber plants with about three foliage leaves were sprayed with the spray liquid until dripping wet. The cucumber plants remained in a greenhouse for 24 hours to dry. They were then, for the purpose of inoculation, dusted with conidia of the fungus *Erysiphe cichoracearum*. The plants were subsequently placed in a greenhouse at 23—24°C and at a relative atmospheric humidity of about 75%.

After 12 days, the infection of the cucumber plants was determined as a percentage of the untreated but also inoculated control plants. 0% means no infection occurred; 100% means that the infection was exactly as great as in the case of the control plants.

The active compounds, the concentrations of the active compounds and the results can be seen from the following table:

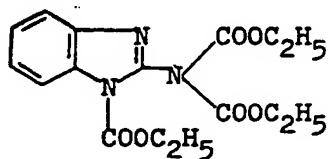
T a b l e*Erysiphe* test

| Active compound | Infection in % of the infection of the untreated control at an active compound concentration of 0.00125% |
|-----------------|--|
|-----------------|--|

known:

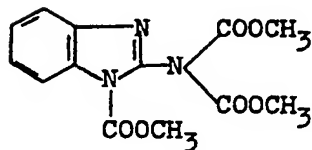
29

(Quinomethionate)

according to the invention:

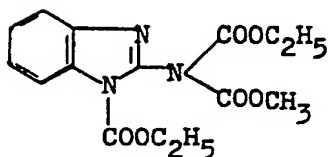
(5)

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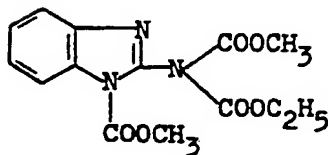
(1)

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(2)

10



(6)

9

Example B.

Erysiphe test/systemic

Solvent: 4.7 parts by weight of acetone

Dispersing agent: 0.3 part by weight of alkylaryl polyglycol ether

Water: 95 parts by weight

The amount of active compound required for the desired active-compound concentration in the watering liquid was mixed with the stated amount of the solvent and the concentrate was diluted with the stated amount of water, which contained the stated additives.

5 Cucumber plants grown in standard soil were watered, in the 1 to 2-leaved stage, once a week with 20 ml of the watering liquid, containing the stated concentration of active compound, per 100 ml of soil. 5

10 After the treatment, the plants thus treated were inoculated with conidia of the fungus *Erysiphe cichoracearum*. Thereafter the plants were placed in a greenhouse at 23—24°C and a relative atmospheric humidity of 70%. After 12 days, the infection of the cucumber plants was determined in per cent of the untreated but also inoculated control plants. 10

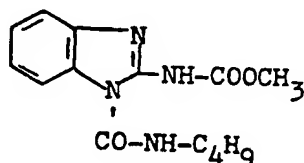
0% denotes that no infection occurred and 100% means that the infection was exactly as great as in the case of the control plants.

15 The active compounds, active compound concentrations and results can be seen from the table which follows: 15

T a b l e B

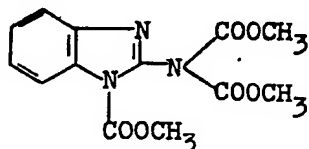
| Active compound | Infection in % of the infection of the untreated control at an active compound concentration of 5 ppm |
|-----------------|---|
|-----------------|---|

known:



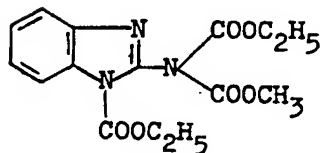
100

according to the invention:



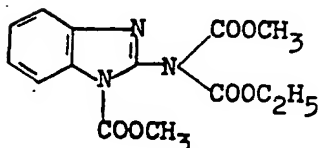
(1)

4



(2)

31



(6)

27

Example C.

Powdery mildew of barley test (*Erysiphe graminis* var. *hordei*/systemic) (fungal disease of cereal shoots)

5 The active compounds were used as pulverulent seed-treatment agents. They were produced by extending the particular active compound with a mixture of equal parts by weight of talc and kieselguhr to give a fine pulverulent mixture having the desired concentration of active compound. 5

10 For the treatment of the seed, barley seed was shaken with the extended active compound in a closed glass bottle. The seed was sown at the rate of 3×12 grains in flowerpots, 2 cm deep in a mixture of one part by volume of Frukotorfer standard soil and one part by volume of quartz sand. Germination and emergence took place under favourable conditions in a greenhouse. 7 days after sowing, when the barley plants had developed their first leaf, they were dusted with fresh spores of *Erysiphe graminis* var. *hordei* and cultivated at 21—22°C and 70% relative atmospheric humidity and 16 hours' exposure to light. Within 6 days, the typical mildew pustules formed on the leaves. 10 15

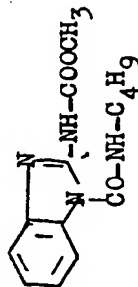
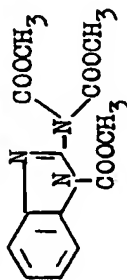
20 The degree of infection is expressed as a percentage of the infection of the untreated control plants. Thus, 0% denotes that no infection occurred and 100% denotes that the degree of infection was as in the case of the untreated control. The more active the active compound, the lower was the infection by mildew. 20

The active compounds, active-compound concentrations in the seed-treatment agent, the amount used of the latter and the percentage infection by mildew can be seen from the table which follows.

T a b l e 0

Powdery mildew of barley test (*Erysiphe graminis* var. *hordei*)/systemic

| Active compounds | Active-compound concentration in the dressing, in % by weight | Amount of dressing used in g/kg of seed | Infection in % of the untreated control |
|-----------------------------|---|---|---|
| without dressing | - | - | 100 |
| according to the invention: | | | |
| (1) | 30 | 2 | 0.0 |
| | 30 | 3.3 | 0.0 |
| | 30 | 10 | 0.0 |
| known: | | | |
| | 30 | 2 | 40.6 |
| | 30 | 3.3 | 25.0 |
| | 30 | 10 | 6.3 |



Example D.

Podospheera test/systemic

Solvent: 4.7 parts by weight of acetone
 Dispersing agent: 0.3 part by weight of alkylaryl polyglycol ether
 Water: 95 parts by weight

The amount of active compound required for the desired concentration of the active compound in the watering liquid was mixed with the stated amount of solvent and the concentrate was diluted with the stated amount of water which contained the stated additions.

Apple seedlings grown in standard soil, in the 3 to 4-leaved stage, were watered once within a week with 20 ml of the watering liquid, having the stated concentration of active compound, per 100 ml of soil. After the treatment, the plants treated in this way were inoculated with conidia of *Podosphaera leucotricha* Salm. and placed in a greenhouse at a temperature of 21—23°C and a relative atmospheric humidity of about 70%.

10 days after the inoculation, the infection of the seedlings was determined as a percentage of the untreated but also inoculated control plants. 0% means that no infection occurred and 100% means that the infection was exactly as great as in the case of the control plants.

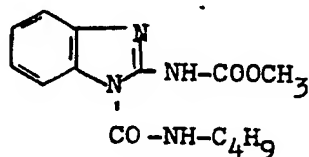
The active compounds, the concentrations of the active compounds and the results can be seen from the table which follows:

T a b l e D

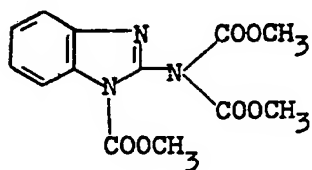
Podosphaera test/systemic

| Active compound | Infection in % of the infection of the untreated control at an active compound concentration of 25 ppm |
|-----------------|--|
|-----------------|--|

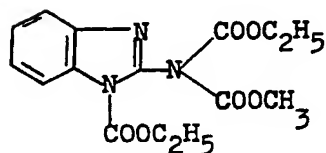
known



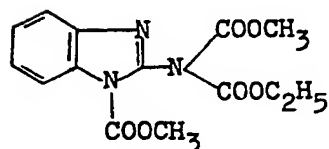
according to the invention:



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Example E.

Fusicladium test/systemic

Solvent: 4.7 parts by weight of acetone

Emulsifier: 0.3 part by weight of alkylaryl polyglycol ether

Water: 95 parts by weight

The amount of active compound required for the desired concentration of the active compound in the watering liquid was mixed with the stated amount of solvent and the concentrate was diluted with the stated amount of water which contained the stated additions.

Apple seedlings grown in standard soil, in the 3 to 4-leaved stage, were watered once within a week with 20 ml of the watering liquid, having the stated concentration of active compound, per 100 ml of soil.

After the treatment, the plants treated in this way were inoculated with an aqueous conidia suspension of *Fusicladium dendriticum* Fuckel and incubated for 18 hours in a humidity chamber at 18—20°C and 100% relative atmospheric humidity. The plants were then again placed in the greenhouse, for 14 days.

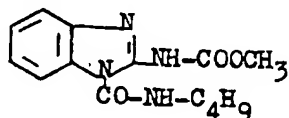
15 days after the inoculation, the infection of the seedlings was determined in % of the infection of the untreated but also inoculated control plants. 0% denotes that no infection occurred and 100% denotes that the infection was exactly as great as in the case of the control plants.

The active compounds, the concentration of the active compounds and the results can be seen from the table which follows:

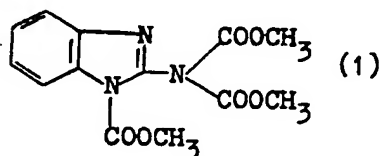
Table E

Fusicladium test/systemic

| Active compound | Infection in % of the infection of the untreated control at an active compound concentration of 30 ppm |
|-----------------|--|
|-----------------|--|

known:

29

according to the invention:

10

Example F.

Fusicladium test (apple scab) [Curative]

Solvent: 4.7 parts by weight of acetone

Emulsifier: 0.3 part by weight of alkylaryl polyglycol ether

Water: 95 parts by weight

The amount of active compound required for the desired concentration of the active compound in the spray liquid was mixed with the stated amount of solvent, and the concentrate was diluted with the stated amount of water which contained the stated additions.

Young apple seedlings in the 4 to 6-leaved stage were inoculated with an aqueous conidium suspension of the apple scab causative organism (*Fusicladium dendriticum* Fuckel) and incubated for 18 hours in a humidity chamber at 18—20°C and at a relative atmospheric humidity of 100%. The plants were then brought into a green-

house and dried.

After standing for a suitable period of time, the plants were sprayed until dripping wet with the spray liquid prepared in the manner described above. The plants were then again brought into a greenhouse.

15 days after inoculation, the infection of the apple seedlings was determined as a percentage of the untreated but also inoculated control plants.

0% means that no infection occurred; 100% means that the infection was exactly as great as in the case of the control plants.

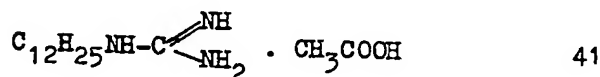
The active compounds, the concentrations of the active compounds, the period of time between inoculation and spraying and the results obtained can be seen from the following table:

T a b l e F

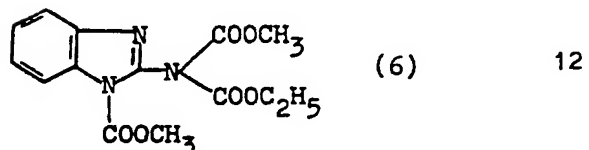
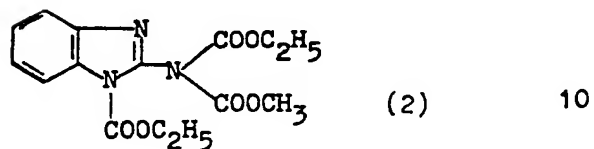
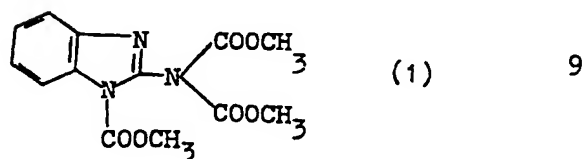
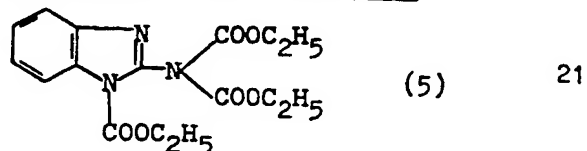
Fusicladium test [apple scab] curative

| Active compound | Dwell time in hours | Infection in % of the infection of the untreated con- trol at an active compound concen- tration (in %) of 0.0025 |
|-----------------|------------------------|---|
|-----------------|------------------------|---|

known:



according to the invention:



Example G.

Bacteria test/*Xanthomonas oryzae*

Solvent: 1.9 parts by weight of DMF

Dispersing agent: 0.1 part by weight of alkylaryl polyglycol ether

Water: 98 parts by weight

The amount of active compound required for the desired concentration of active compound in the spray liquid was mixed with the stated amount of the solvent and of the dispersing agent and the concentrate was diluted with the stated amount of water.

30 rice plants which were about 30 days old were sprayed with the spray liquid until dripping wet. The plants remained in a greenhouse at temperatures of 22—24°C and a relative atmospheric humidity of about 70% until they were dry. Thereafter, needles were dipped into an aqueous bacteria suspension of *Xanthomonas oryzae* and the plants were inoculated by pricking the leaves. After inoculation, the plants were left in a room at 26—28°C and 80% relative atmospheric humidity.

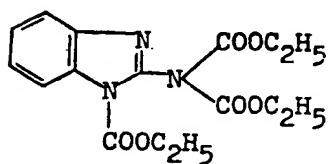
10 days after the inoculation, the infection was determined for all leaves which had been injured by pricking, inoculated and treated beforehand with the preparation, as a percentage of the untreated but also inoculated leaves of the control plants. 0% denotes that no infection occurred and 100% denotes that the infection was just as great as in the case of the control plants.

The active compounds, active compound concentrations and results can be seen from the table which follows.

Table G

Bacteria test/*Xanthomonas oryzae*

| Active compound | Infection in % of the infection of the untreated control at an active compound concentration (in %) of | |
|-------------------|--|-------|
| | 0.05 | 0.025 |
| Untreated control | 100 | |



(5)

13

25

Example H.

Fusicladium test/systemic

Solvent: 4.7 parts by weight of acetone

Emulsifier: 0.3 part by weight of alkylaryl polyglycol ether

Water: 95 parts by weight.

The amount of active compound required for the desired concentration of the active compound in the watering liquid was mixed with the stated amount of solvent and the concentrate was diluted with the stated amount of water which contained the stated additions.

Apple seedlings grown in standard soil, in the 3 to 4-leaved stage, were watered once within a week with 20 ml of the watering liquid, having the stated concentration of active compound, per 100 ml of soil.

After the treatment, the plants treated in this way were inoculated with an aqueous conidia suspension of *Fusicladium dendriticum* Fuckel and incubated for 18 hours in a humidity chamber at 18—20°C and 100% relative atmospheric humidity. The plants are then again placed in the greenhouse, for 14 days.

15 days after the inoculation, the infection of the seedlings was determined in % of the infection of the untreated but also inoculated control plants. 0% means that no

infection occurred and 100% denotes that the infection was exactly as great as in the case of the control plants.

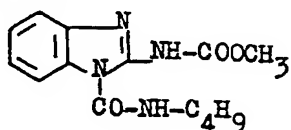
The active compounds, the concentration of the active compounds and the results can be seen from the table which follows:

T a b l e H

Fusicladium test/systemic

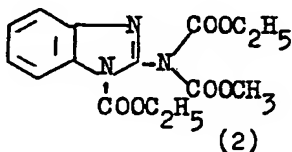
| Active compound | Infection in % of the infection of the untreated control at an active compound concentration of 12.5 ppm |
|-----------------|--|
|-----------------|--|

known:

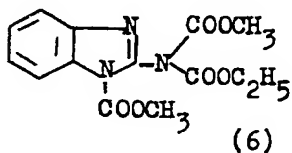


22

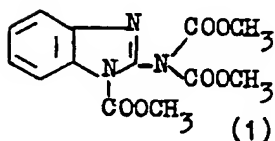
according to the invention:



9



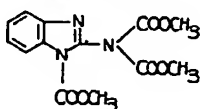
2



1

The preparation of the compounds according to the present invention is illustrated in the following Examples.

Example 1.



(1)

10

(a) 42 g (0.45 mole) of chlorocarbonic acid methyl ester were added dropwise to 13.3 g (0.1 mole) of 2-amino-benzimidazole in 50 ml of pyridine at 25°C, in the course of which the temperature rose to 35°C. After 1 hour, about 300 ml of water were allowed to run in and the colourless crystals which had precipitated were filtered off. After recrystallisation from ethyl acetate, 21 g (70% of theory) of 1-methoxycarbonyl-2-[bis-(methoxycarbonyl)-amino]-benzimidazole of melting point 149—151°C were obtained.

10

15

15

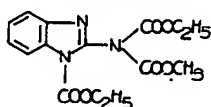
(b) 40 g (0.3 mole) of pyrocarbonic acid dimethyl ester were added dropwise at 20—25°C to 19.1 g (0.1 mole) of 2-methoxycarbonyl-amino-benzimidazole in 50 ml of pyridine. After 2 hours, about 350 ml of water were run in and the product which had precipitated was isolated by filtration. After drying, the product was dissolved in 100 ml of chloroform, a slight amount of residue of starting material was filtered off, and evaporation *in vacuo* yielded 15 g (49% of theory) of 1-methoxycarbonyl-2-[bis-(methoxycarbonyl)-amino]-benzimidazole of melting point 149—151°C.

2-Methoxycarbonylamino-benzimidazole, used as the starting material, is known (see United States Patent Specification 2,933,504, Example 2).

(c) 295 g (2.2 moles) of pyrocarbonic acid diethyl ester were added dropwise over the course of 2.5 hours to 249 g (1 mole) of 1-methoxycarbonyl-2-methoxycarbonyl-amino-benzimidazole in 750 ml of pyridine at 20—30°C. The mixture was stirred for a further hour, about 2 litres of petroleum ether were added and the crystalline product was filtered off. After recrystallisation from ethyl acetate, 244 g (79% of theory) of 1-methoxycarbonyl-2-[bis-(methoxycarbonyl)-amino]-benzimidazole of melting point 149—151°C were obtained.

1-Methoxycarbonyl-2-methoxycarbonylamino-benzimidazole, used as the starting material, is known (see United States Patent Specification 2,933,504, Example 2).

Example 2.

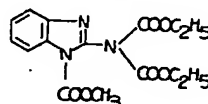


(2)

27 g (0.2 mole) of pyrocarbonic acid dimethyl ester were added dropwise to 27.7 g (0.1 mole) of 1-ethoxycarbonyl-2-ethoxycarbonyl-amino-benzimidazole in 75 ml of pyridine, in the course of which the temperature rose to 40°C. The mixture was stirred for a further 2 hours at room temperature and was evaporated *in vacuo*. Recrystallisation of the residue from ligroin/ethanol (9:1) yielded 18.5 g (55% of theory) of 1-ethoxycarbonyl-2-(N-methoxycarbonyl-N-ethoxycarbonylamino)-benzimidazole, of melting point 71—72°C.

1-Ethoxycarbonyl-2-ethoxycarbonylamino-benzimidazole, used as the starting material, is known (see United States Patent Specification 2,933,504, Example 16).

Example 3.

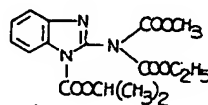


(3)

17 g (0.15 mole) of chlorocarbonic acid ethyl ester were added dropwise to 26.3 g (0.1 mole) of 1-methoxycarbonyl-2-ethoxycarbonyl-amino-benzimidazole in 75 ml of pyridine at 20—25°C. After 1 hour, about 300 ml of water were allowed to run in and the crystals which had precipitated were isolated by filtration. After recrystallisation from ethanol, 28.5 g (85% of theory) of 1-methoxycarbonyl-2-[bis-(ethoxycarbonyl)-amino]-benzimidazole, of melting point 108—110°C, were obtained.

1-Methoxycarbonyl-2-ethoxycarbonylamino-benzimidazole, used as the starting material, is known (see United States Patent Specification 2,933,504, Example 15).

Example 4.



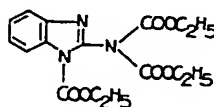
(4)

10 g (0.075 mole) of pyrocarbonic acid dimethyl ester were added dropwise at 15—20°C to 19 g (0.065 mole) of 1-isopropoxycarbonyl-2-ethoxycarbonyl-amino-benzimidazole in 50 ml of pyridine. After 2 hours, about 300 ml of water were allowed to run in and the product formed was filtered off. After drying and recrystallisation

from cyclohexane, 12.5 g (55% of theory) of 1-isopropoxycarbonyl-2-(N-methoxycarbonyl-N-ethoxycarbonyl-amino)-benzimidazole were obtained in the form of colourless crystals of melting point 103—104°C.

- 5 1-Isopropoxycarbonyl-2-ethoxycarbonylamino-benzimidazole (melting point 94—95°C/cyclohexane), used as the starting material, can be prepared from 2-ethoxycarbonylamino-benzimidazole and chlorocarbonic acid isopropyl ester (analogously to the procedure in United States Patent Specification 2,933,504, Example 15).

Example 5.



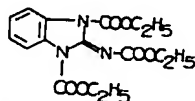
(5)

- 10 (a) 33 g (0.3 mole) of chlorocarbonic acid ethyl ester were added dropwise to 20.5 g (0.1 mole) of 2-ethoxycarbonyl-amino-benzimidazole in 75 ml of pyridine at 20—25°C. After 1 hour, 1 litre of water was allowed to run in, whereby an oil was obtained which became crystalline after a short time. After filtration, washing with water and drying, 30 g (86% of theory) of 1-ethoxycarbonyl-2-[bis-(ethoxycarbonyl)-amino]-benzimidazole of melting point 69—70°C were obtained.

15 2-Ethoxycarbonylamino-benzimidazole, used as the starting material, is known (see United States Patent Specification 2,933,504, Example 15).

- 20 (b) 33 g (0.3 mole) of chlorocarbonic acid ethyl ester were added dropwise to 20.5 g (0.1 mole) of 1-ethoxycarbonyl-2-amino-benzimidazole in 70 ml of pyridine at 20—25°C. After 1.5 hours, about 350 ml of water were allowed to run in and the product which had precipitated was filtered off and rinsed with water and subsequently with benzene. After drying, 16 g (46% of theory) of 1-ethoxycarbonyl-2-[bis-(ethoxycarbonyl)-amino]-benzimidazole of melting point 69—70°C were obtained.

25 From the evaporation residue of the benzene used for washing, 7 g (20% of theory) of the isomeric compound 1,3-bis(ethoxycarbonyl)-2-ethoxycarbonylimino-benzimidazoline of the formula



(5a)

of melting point 123—125°C were obtained by recrystallisation from ligroin.

- 30 The isomeric compounds (5) and (5a) can be distinguished unambiguously by means of their ¹H nuclear resonance spectrum.

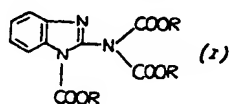
35 1-Ethoxycarbonyl-2-amino-benzimidazole (melting point 205°C, with transformation to a product which then melts at 315°C), which is used as the starting material, can be prepared from 2-amino-benzimidazole and chlorocarbonic acid ethyl ester (analogously to the procedure in United States Patent Specification 2,933,502, Example 1).

- 40 (c) 356 g (0.33 mole) of chlorocarbonic acid ethyl ester were added dropwise to 133 g (1 mole) of 2-amino-benzimidazole in 750 ml of pyridine at 0° to 5°C. The mixture was stirred for a further hour and first the 1,3-bis-(ethoxycarbonyl)-2-ethoxycarbonylimino-benzimidazoline (5a) formed as a by-product was isolated by filtration. After washing with water and recrystallisation from ethanol, 70 g (20% of theory) of the compound (5a) were obtained in the form of colourless crystals of melting point 123—125°C.

45 On evaporation of the pyridine mother liquor *in vacuo*, a residue remained from which 200 g (57% of theory) of 1-ethoxycarbonyl-2-[bis-(ethoxycarbonyl)-amino]-benzimidazole (5) were isolated, in the form of colourless crystals of melting point 69—70°C, by treatment with water, filtration and recrystallisation.

WHAT WE CLAIM IS:—

1. 1-Alkoxycarbonyl-2-[bis-(alkoxycarbonyl)-amino]-benzimidazoles of the general formula

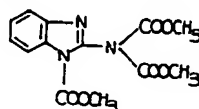


in which

R is alkyl with 1—4 carbon atoms, it being possible for the radicals R to be different from one another or two or three radicals R to be identical.

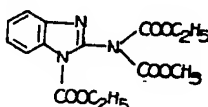
2. Compounds according to claim 1, in which R is methyl, ethyl, n-propyl, isopropyl or n-butyl.

3. The compound of the formula



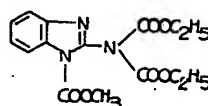
(1)

4. The compound of the formula



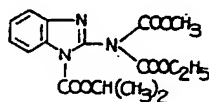
(2)

5. The compound of the formula



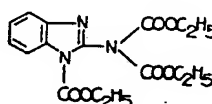
(3)

6. The compound of the formula



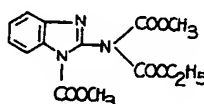
(4)

7. The compound of the formula



(5)

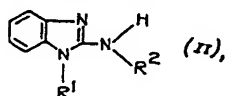
8. The compound of the formula



(6)

9. A process for the preparation of a 1-alkoxycarbonyl-2-[bis-(alkoxycarbonyl)-amino]-benzimidazole according to any of claims 1 to 8, in which a 2-amino-benzimidazole of the general formula

20



in which

R¹ and R² are each hydrogen or a —COOR radical, and
R has the meaning stated in claim 1,

is reacted with a carbonic acid derivative of the general formula



(III),

in which

X is halogen or an —O—COOR radical, and
R has the meaning stated in claim 1,

optionally in the presence of a diluent and optionally in the presence of an acid-binding agent.

10. A process according to claim 9, in which X is chlorine.

11. A process according to claim 9 or 10, in which the reaction is effected in an inert polar solvent.

12. A process according to claim 11, in which the solvent is pyridine.

13. A process according to any of claims 9 to 12, in which the reaction is effected at from -10° to +100°C.

14. A process according to claim 13, in which the reaction is effected at from 10° to 50°C.

15. A process according to any of claims 9 to 14, in which the 2-amino-benzimidazole (II) is one that is hereinbefore specifically named.

16. A process according to any of claims 9 to 15, in which the carbonic acid derivative (III) is one that is hereinbefore specifically named.

17. A process according to any of claims 9 to 16, in which the 2-amino-benzimidazole (II) and carbonic acid derivative (III) are used in a molar ratio of 1:3—4.5 (when R¹ and R² are both hydrogen), 1:2—3.5 (when either R¹ or R² is a —COOR radical) or 1:1—2.5 (when R¹ and R² are both —COOR radicals).

18. A process for the preparation of a compound according to claim 1, substantially as hereinbefore described in any of Examples 1 to 5.

19. Compounds according to claim 1, whenever prepared by a process according to any of claims 9 to 18.

20. A fungicidal or bactericidal composition containing as active ingredient a compound according to any of claims 1 to 5 and 19 in admixture with a solid or liquefied gaseous diluent or carrier or in admixture with a liquid diluent or carrier containing a surface-active agent.

21. A composition according to claim 20 containing from 0.1 to 95% of the active compound, by weight.

22. A composition according to claim 21 containing from 0.5 to 90% of the active compound, by weight.

23. A method of combating fungi or bacteria which comprises applying to the fungi or bacteria or a habitat thereof a compound according to any of claims 1 to 8 and 19 alone or in the form of a composition containing as active ingredient a compound according to any of claims 1 to 8 and 19 in admixture with a diluent or carrier.

24. A method according to claim 23 in which a composition is used containing from 0.0001 to 10% of the active compound, by weight.

25. A method according to claim 24 in which a composition is used containing from 0.01 to 1% of the active compound, by weight.

26. A method according to any of claims 23 to 25 in which the active compound is applied to seed in an amount of 0.1 to 10 g per kg of seed.

27. A method according to any of claims 23 to 24 in which the active compound is applied to soil in an amount of 1 to 500 g per cubic metre of soil.

28. A method according to any of claims 23 to 27 in which the active compound is one of those hereinbefore mentioned in any of Examples A to H.

29. Crops protected from damage by fungi or bacteria by being grown in areas in which immediately prior to and/or during the time of the growing a compound according to any of claims 1 to 8 and 19 was applied alone or in admixture with a diluent or carrier.

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